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| TDC Form Similar to: Form PTO-1390] | | U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE | | ATTORNEY DOCKET NUMBER 44114 | |
| TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371 | | | | U.S. APPLICATION NO. (if known, see 37 C.F.R. 1.5) <div style="font-size: 1.5em; font-weight: bold; text-align: center;">09/890907</div> | |
| INTERNATIONAL APPLICATION NO. PCT/US00/03682 | | INTERNATIONAL FILING DATE 11 February 2000 | | PRIORITY DATE CLAIMED 12 February 1999 | |
| TITLE OF INVENTION NANOCOMPOSITE ARTICLES AND PROCESS FOR MAKING | | | | | |
| APPLICANT(S) FOR DO/EO/US Richard F. Fibiger; Kyung W. Suh; Mark A. Barger; Joseph A. Schomaker; Wenbin Liang; George A. Mackey | | | | | |
| <p>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> has been transmitted by the International Bureau. c. <input checked="" type="checkbox"/> is not required, as the application was filed in the United States receiving Office (RO/US). 6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> A translation of the Annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). <p>Items 11. to 15. below concern other document(s) or information included:</p> <ol style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> A FIRST preliminary amendment. <li style="padding-left: 20px;"><input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 13. <input type="checkbox"/> A substitute specification. 14. <input type="checkbox"/> A change of power of attorney and/or address letter. 15. <input type="checkbox"/> Other items or information: | | | | | |

06 AUG 2001

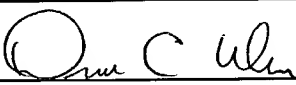
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| U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.50) <div style="font-size: 1.5em; font-weight: bold; text-align: center;">09/890907</div> | | INTERNATIONAL APPLICATION NO. PCT/US00/03682 | | ATTORNEY'S DOCKET NUMBER 44114 | |
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|--|--------------|--------------|------------|------------------------------|--|
| 17. <input checked="" type="checkbox"/> The following fees are submitted: <div style="margin-left: 20px;"> Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO \$ 860.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) \$ 690.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$ 710.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445 (a)(2)) paid to USPTO \$ 1,000.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$ 100.00 </div> <div style="text-align: right; margin-top: 10px;"> ENTER APPROPRIATE BASIC FEE AMOUNT = </div> | | | | CALCULATIONS PTO USE ONLY | |
| | | | | \$ 860.00 | |
| Surcharge of \$ 130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)). | | | | \$ 130.00 | |
| Claims | Number Filed | Number Extra | Rate | | |
| Total Claim | 10 - 20 = | 0 | X \$ 18.00 | \$ 0.00 | |
| Independent Claims | 1 - 3 = | 0 | X \$ 80.00 | \$ 0.00 | |
| Multiple dependent claim(s) (if applicable) | | | | \$ 270.00 | |
| Processing fee of \$ 0 for furnishing the English Translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | | | | \$ 0.00 | |
| TOTAL NATIONAL FEE = | | | | \$ 1,260.00 | |
| | | | | Amount to be refunded: \$ | |
| | | | | charged: \$ | |

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| a. <input type="checkbox"/> | A check in the amount of \$ _____ to cover the above fees is enclosed. |
| b. <input checked="" type="checkbox"/> | Please charge my Deposit Account No. 04-1512 in the amount of \$ 1,260.00 to cover the above fees. A duplicate copy of this sheet is enclosed. |
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Note: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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| SEND ALL CORRESPONDENCE TO: Graham E. Taylor The Dow Chemical Company Intellectual Property P.O. Box 1967 Midland, Michigan 48641-1967 UNITED STATES OF AMERICA Phone: (979)238-1638 | Signature: <u></u> <div style="text-align: center;">Duane C. Ulmer</div> , Registration No. 34,941 Date: <u>06 August 2001</u> |
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JC20 Rec'd PCT/PTO 06 AUG 2001

09/890907

EXPRESS MAIL MAILING LABEL NO. EL413490808US

DATE OF DEPOSIT: August 6, 2001

**THIS APPLICATION IS THE ENTRY INTO THE
NATIONAL PHASE UNDER 35 U.S.C. 371**

Applicant(s): Richard F. Fibiger; Kyung W. Suh; Mark A. Barger; Joseph A. Schomaker; Wenbin Liang; George A. Mackey

International Application No. PCT/US00/03682

International Filing Date: 11 February 2000

Priority Date Claimed: 12 February 1999

Title: NANOCOMPOSITE ARTICLES AND PROCESS FOR MAKING

Attorney's Docket No.: 44114

NANOCOMPOSITE ARTICLES AND PROCESS FOR MAKING

This application is under a United States Government contract with The Department of Commerce (NIST)-Advanced Technology Program Project #70NANB7H3028.

5 BACKGROUND

This invention relates to polymer systems reinforced with delaminated or exfoliated multi-layered silicates, that is, nanocomposite polymer systems.

10 Nanocomposite polymers are compositions comprising a relatively high number (but relatively low weight) of exfoliated multi-layered silicate material dispersed in a given volume of continuous polymer matrix, United States Patent 5,717,000 to Seema V. Karande, Chai-Jing Chou, Jitka H. Solc and Kyung W. Suh, herein fully incorporated by reference. As discussed in the '000 patent and as is well known in the art, nanocomposite polymers exhibit many increased physical property enhancements at a much lower volume percent of filler than conventionally filled polymers. For example, when nanocomposite polymers are formed into a film, the exfoliated multi-layered silicate material can be oriented in the direction parallel to the film surface, which contributes to the barrier properties of the film, United States Patent 5,164,460, herein fully incorporated by reference.

15 SUMMARY OF THE INVENTION

20 The instant invention has twelve embodiments. The first embodiment is an improved process for making a structural foamed polymer comprising the steps of dispersing a gas-producing material into a fluid polymer at a first pressure followed by a second pressure less than the first pressure, the difference between the first pressure and the second pressure being sufficient to generate bubbles of gas in the fluid polymer. The improvement comprises the step of dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

30 The second embodiment of the instant invention is an improved structural foamed polymer comprising gas cells having polymer walls. The improvement comprises the polymer having dispersed therein single layers of silicate material, double layers of

silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

5 The third embodiment of the instant invention is an improved process for making a multilayer polymer film or sheet comprising the step of coextruding layers of at least two different polymers or at least two different layers of the same polymer to form the multilayer polymer film or sheet. The improvement comprises the step of dispersing a multi-layered silicate material with at least one polymer so that the at least one polymer has
10 dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

15 The fourth embodiment of the instant invention is an improved multilayer polymer film, sheet or tube comprising layers of at least two different polymers or at least two layers of the same polymer. The improvement comprises at least one polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and
20 more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

25 The fifth embodiment of the instant invention is an improved pultrusion process comprising the steps of impregnating a reinforcing fiber bundle with a polymer and forming a structural profile. The improvement comprises the step of dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of
30 silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

 The sixth embodiment of the instant invention is an improved pultrusion structural profile comprising a reinforcing fiber bundle impregnated with a polymer. The

improvement comprises the polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The seventh embodiment of the instant invention is an improved compression molding process comprising the step of compression molding an extruded fiber reinforced polymer pre-form. The improvement comprises the step of dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The eighth embodiment of the instant invention is an improved article, the article made by compression molding an extruded fiber reinforced polymer pre-form. The improvement comprises the polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The ninth embodiment of the instant invention is an improved process for making strand foamed polymer comprising the steps of extruding a polymer through a plurality of openings to form strands and then coalescing the strands. The improvement comprises the step of dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The tenth embodiment of the instant invention is improved strand foamed polymer article. The improvement comprises the polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of

silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The eleventh embodiment of the instant invention is an improved SCORIM process for molding a polymer into an article comprising the step of introducing the polymer into a mold by reciprocating flow. The improvement comprises the step of dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate.

The twelfth embodiment of the instant invention is an improved SCORIM molded polymer article. The improvement comprises the polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

In each of the above embodiments an important benefit of the instant invention is the orientation of the plane of the layers of silicate material. More specifically, most of the layers of silicate material have substantially the same orientation (within thirty degrees of angle of the major surface of the fabricated material or of the interface of a multilayer structure) and this orientation improves the properties of the product. In the structural foamed polymer embodiment, the orientation is parallel to the cell wall with, for example, about seventy percent of the layers being within thirty degrees of parallel with the cell wall. In the multilayer polymer film, sheet or tube embodiment, the orientation is parallel to major surface of the film, sheet or tube. In the pultrusion embodiment, the orientation is parallel to fiber bundle. In the compression molding embodiment, the orientation is parallel to the reinforcing fibers. In the strand foamed polymer embodiment, the layers of silicate material are partially oriented by the initial extrusion process prior to foaming and further oriented parallel to the cell wall during foaming. In the SCORIM embodiment, the alignment is parallel to the plane of the part being molded. Another important benefit of the instant invention is that its articles can be relatively large (more than one kilogram) in comparison

with articles made according to the prior art. The amount of multi-layered silicate material used in the instant invention is preferably between one and twenty weight percent.

DETAILED DESCRIPTION OF THE INVENTION

The term "multi-layered silicate material" is well known in the nanocomposite art and includes phyllosilicate clays and layered silicates. Illustrative of such materials are smectite clay minerals such as montmorillonite, nontronite, beidellite, hectorite, saponite, sauconite, and vermiculite clay minerals. This term also includes illite minerals such as ledikite and layered silicates such as magadiite and kenyaite. Preferred multi-layered silicate materials are phyllosilicates of the 2:1 type having a negative charge on the layers ranging from 0.25 to 1.5 charges per formula unit and a commensurate number of exchangeable cations in the interlayer spaces. Most preferred are smectite clay minerals such as montmorillonite, nontronite, beidellite, hectorite, saponite, sauconite, and the layered silicates magadiite, and kenyaite.

The technique used to disperse or "exfoliate" a multi-layered silicate material into a polymer is not critical in the instant invention as long as the volume percent of the one, two, three, four and five layers of silicate material so dispersed or "exfoliated" are greater than the volume percent of the more than five layers of silicate material so dispersed or "exfoliated". For example, such dispersion can be accomplished by polymerizing one or more monomers with a treated multi-layered silicate material as described in United States Patent 5,973,053, herein fully incorporated by reference or, for example, by melt blending a treated multi-layered silicate material with a polymer as described in United States Patent 5,385,776, herein fully incorporated by reference. The volume percent of single, double, three, four five and more than five layers of silicate material is determined herein by electron microscopic examination of a representative sample wherein each layer by definition herein has the same volume.

The term "structural foamed polymer" and a basic teaching regarding its process and articles will be found in the Encyclopedia of Polymer Science and Engineering, Vol. 15, 1989, p. 771-797, herein fully incorporated by reference, and is patentably different than the foams discussed in United States Patent 5,717,000. The minimum density of such foam product is often limited by the ability of the cell walls to withstand the loads which are applied during use. Conventional relatively large sized fillers like talc can be used to strengthen the cell walls. However, this can lead to premature rupture of the cell wall when the cell wall thickness approaches the size of the filler particles. This can limit how low a density of foam which can be prepared. In addition, an increase in the melt strength of the

polymer is desirable for thinner cell walls and conventional fillers do not change the melt strength substantially. The orientation of the ideally single platelet shaped nanofillers of the instant invention (and the fact that, once oriented, they project a cross section of less than a few nanometers across the thickness of the cell walls) can overcome these difficulties and lead to lower density foam products with good load bearing capabilities. The high aspect ratio of the nanofillers of the instant invention also dramatically increases the polymer's melt strength and produces compositions in which the cell wall sees the maximum reinforcement both in the melt and solidified state. Thus a lower density foam can be produced which equals the performance of higher density products.

The term "multilayer polymer film, sheet or tube" is defined in and a basic teaching regarding its process and articles will be found in the Encyclopedia of Polymer Science and Engineering, Vol. 7, 1987, p106-127 herein fully incorporated by reference and in United States Patents 3,576,707, 4,122,138, 5,443,874, 5,129,544, 5,441,781, 4,005,967, 3,739,052, 3,947,204 and 3,884,606, each of which are herein fully incorporated by reference. The multilayer coextrusion process has been used commercially to manufacture unique articles, tubes, sheets and films with 3 to 10 layers. It allows manufacture of products with layers thinner than can be made and handled as an individual ply. The layers may individually provide a specific attribute, such as barrier properties, mechanical strength, printability, or adhesion, to the overall structure. The multilayer extrusion process of the instant invention can, of course, be coupled with other processes such as solid phase forming, blow molding, stretch-blow molding, injection-blow molding and thermoforming to produce shaped articles.

The prior art multilayer coextrusion process suffers from difficulties in matching the rheology of separate layers. Mismatched rheology can lead to poor interfacial adhesion, a wavy interface and in extreme cases breakup of the interface. Thus, poor optical properties and reduced physical properties can be produced. It would also be advantageous to reduce the thickness of the individual layers in order to save on material costs. Reduction in thickness requires improved performance as well as very uniform layer structures. Conventional relatively large sized fillers such as talc can not generally be used in layers below 50 micrometers in thickness because such conventional fillers produce defects and flow instabilities. Extrusion molding processes often provide improved strength in the machine (extrusion) direction but are much weaker in the cross-direction. Mechanical processes such as molding with rotation have been developed to overcome this problem but

they require specialized additional equipment. A simple method for maintaining strength biaxially is desired.

In this embodiment of the instant invention it is found that the ease of orientation of the plate-like nanofillers provides a method to optimize the properties in both thin layers and in relatively thick layers in a multilayer coextruded article. The plate-like nanofillers of the instant invention provide added melt strength to low viscosity layers which leads to more uniform layer thickness, are small enough so that they do not disrupt even the thinnest single layer and the formation process causes a high degree of orientation of the plates thus maximizing the performance of the article produced. The small size of the plates makes them transparent so that they can be used in applications where clarity is required. The biaxial nature of the platelet reinforcement provides additional strength in the cross-direction, which is inherently weak due to the fabrication process.

The composites of this embodiment of the instant invention are particularly applicable in multilayer automotive fuel tanks, automotive gas filler tube/neck, fuel transport lines and hollow multilayer moldings such as carbonated beverage bottles. In these situations, the nanofillers of the instant invention may be incorporated into those layers responsible for the desired property, for example, barrier to gases or vapors. The nanofiller of the instant invention provides improved performance and clarity; the orientation imparted to the nanoparticles in the extrusion process maximizes the performance. In the case of fuel tanks or other large articles, the multilayer sheet may be extruded, followed by thermoforming of separate halves and welding of the halves together to make a completed structure. In the case of other large articles a multilayered tube (or "parison") can be extruded followed by blow molding or the parison into a mold of the desired shape. Sagging of the parison during extrusion and prior to blow molding can cause difficulties in reproducibly controlling the process. The high aspect ratio of the nanofiller provides substantial reinforcement of the polymer melt and thus reduces the sagging problem of a large parison. Other applications of this embodiment of the instant invention include semi-rigid containers for food and industrial materials, signage, machine and furniture side panels and appliances. The number of layers can be five to ten or more than ten layers. In addition, the article made can be more than one kilogram in weight.

Coextrusion has been used commercially to manufacture unique films, sheets and tubes consisting of from as few as 3 layers to thousands of layers where the individual layers can be less than 100 nanometers thick. The plate-like fillers are highly oriented in these films by the extrusion process which assists in the flow stability during extrusion thus

producing more intact layers. The thinner the layers, the greater the orientation and thus the greater the reinforcement. The orientation of the nanofiller also improves barrier and overall mechanical performance. Unlike conventional fillers, the thinness of the nanofillers of the instant invention allows for their presence without interfering with the optical properties of the films (or sheets or tubes).

Applications of this embodiment of the instant invention include barrier packaging for food and drugs, decorative films, nonmetallic mirrors for automotive and construction applications, transparent ultra violet or infra red reflective surfaces for windows and so forth.

The term "pultrusion" is defined in and a basic teaching regarding its process and articles will be found in the Encyclopedia of Polymer Science and Engineering, Vol. 4, 1986, p. 3-9 and 34-36 which are herein fully incorporated by reference. The practice of these processes can produce low modulus in a direction perpendicular to the fiber direction (off axis) and poor performance due to a loss in bonding between the reinforcing fibers and the matrix material. The loss in bonding, which is attributed to a mismatch in the coefficient of thermal expansion (CLTE) between the reinforcing fibers and the matrix resin, can be particularly poor with carbon fibers.

It is an object of this embodiment of the instant invention to improve the off axis strength of the composite via nanocomposites with the high aspect ratio platelets. This improved performance can be more pronounced as the thickness of the composite is reduced due to the alignment of the nanocomposite plates via the shear induced in the pultrusion process. The reduction in the CLTE of the matrix due to the presence of the nanofiller produces a better match of CLTE's between carbon fibers and the matrix resin leading to a more intact interface. This performance is surprising because it tends not to take place with conventional filler materials such as talc or calcium carbonate. This embodiment of the instant invention can be used with thermoplastic and thermoset resins but is most often practiced with thermoset resin like epoxies, vinyl esters, vinyl ethers and urethanes. Applications include, for example, intermodal containers, building walls and panels, structural profiles for bridges, automotive body panels, auto door panels/modules and auto bumper beams.

The term "compression molding" is defined in and a basic teaching regarding its process and articles will be found in the Encyclopedia of Polymer Science and Engineering, Vol. 4, 1986, p. 79-85, 104 and 108 which are herein fully incorporated by

reference. A major problem with parts having support ribs which are made by compression molding an extruded fiber reinforced polymer pre-form can be "show through" of the support ribs when the wall thickness of the part is reduced below about 2 millimeters.

The use of a nanocomposite of the instant invention in the extruded fiber reinforced polymer pre-form reduces rib "show through" by reducing the coefficient of thermal expansion of the polymer to more closely match that of the glass fibers. The extrusion process can optimize orientation of the dispersed nanofiller of the instant invention by the use of multi-slit dies. Thus, the coefficient of linear expansion (CLTE) reduction is optimized by the extrusion process. The use of a nanocomposite of the instant invention can also produce a class A finish of the article superior to the use of conventional filler materials. This embodiment of the instant invention is especially useful to make automotive parts such as door panels, side panels, front end modules and structural instrument panels modules.

The term "strand foamed polymer" is defined in and a basic teaching regarding its process and articles will be found in United States Patents 5,527,573, 4,801,484, 5,206,082 and 4,824,720, each of which are herein fully incorporated by reference. The density of strand foams can be further reduced over standard foams using nanocomposites because the nanofiller plates of the instant invention are optimally oriented by the initial fiber extrusion process prior to foaming. Unlike conventional fillers, the small size of the nanofiller of the instant invention makes this added thinning of the cell wall possible. The added orientation of the nanofiller of the instant embodiment also improves the polymer's melt rheology leading to improved foam stability. The resulting higher dimensional stability and impact strength makes the foams prepared according to this embodiment well suited for automobile bumpers, headliners, insulation panels and interior automobile pillars.

The term "SCORIM" (Shear Controlled Orientation in Injection Molding) is defined in and a basic teaching regarding its process and articles will be found in United States Patents 4,994,220, 5,059,368, 4,925,161 and 5,160,466, each of which are herein fully incorporated by reference. The unique properties of the plate-like nanofiller of the instant invention produces a high degree of alignment across a large cross-section with minimal randomization of the particles, even during a prolonged cooling cycle. Thus larger parts are possible via SCORIM injection molding. In addition the nanofillers of the instant invention can be used for both reinforcement and rheology modification of one or more of the layers in an injection or a co-injection molded part. Applications of this embodiment of the

instant invention include refrigerator liners, automotive facia, containers and washing machine tubs.

EXAMPLE 1

Coextruded films of nanocomposite polyolefin compounds are prepared using a coextrusion line that consists of two 19 millimeter single screw extruders equipped with gear pumps (1.2 cc/revolution pumping capacity). These extruders provide two independent meltstreams into a coextrusion feedblock that provides an initial two-layer meltstream (i.e., the first composite stream). This first composite stream is subsequently passed through a series of two channel layer multipliers (similar in design to those taught by Schrenk, et al. in U.S. 5,202,074, herein fully incorporated by reference) to create a second composite stream having an increased number of layers in accordance with the following equation:

$$N = 2(2^n)$$

Where: N = Total number of layers

n = Number of layer multiplication stages

The second composite stream is subsequently passed through a 350 millimeter wide flex lip die and onto a chilled casting drum to fabricate a thin film.

The materials utilized are Engage EG8200 Brand Polyolefin Elastomer from Dupont-Dow Elastomers; PRIMACOR 3460 Brand Poly(ethylene-co-acrylic acid) from The Dow Chemical Company; PRIMACOR 1430 Brand Poly(ethylene-co-acrylic acid) from The Dow Chemical Company; and Claytone HY Brand quaternary ammonium treated montmorillonite multi-layered silicate material from Southern Clay Products.

The two PRIMACOR grades and Claytone HY are precompounded using a Werner Pfleiderer ZSK30 co-rotating twin screw extruder in the follow weight ratios:

| Material | wt% |
|---------------|-----|
| PRIMACOR 1430 | 80 |
| PRIMACOR 3460 | 16 |
| Claytone HY | 4 |

This compound (Compound "A", approximately 0.8 volume % multi-layered silicate) is then coextruded with the Engage (equal volumetric ratios) using the previously described process under the following conditions:

5 Extruder A

Material: Engage EG8200

Extruder Barrel Set temperatures (C)

Zone 1: 160

Zone 2: 185

10 Zone 3: 200

Gear Pump temperature: 200 C

Extruder Screw Speed: 70 RPM

Pump Speed: 35 RPM

15 Extruder B

Material: Compound A

Extruder Barrel Set temperatures (C)

Zone 1: 155

Zone 2: 175

20 Zone 3: 190

Gear Pump temperature: 190 C

Extruder Screw Speed: 70 RPM

Pump Speed: 35 RPM

25 Layer Multipliers temperature: 192 C

Die temperature: 220 C

The extruded films (nominal 2.5 mil thickness) were then tested for oxygen permeability and specular light transmission in accordance with ASTM test methods D3985 and D1003

30 respectively. The results are shown in the following table:

| Sample | Composition (volume %) | | Multiplication Stages | Total Number of Layers | O ₂ Transmission Rate^ | Percent Haze |
|--------|------------------------|------------|--------------------------|---------------------------|--------------------------------------|-----------------|
| | EG8200 | Compound A | | | | |
| 1 | 50 | 50 | 2 | 8 | 500 | 7 |
| 2 | 50 | 50 | 4 | 32 | 500 | 7 |
| 3 | 50 | 50 | 4 | Blend* | 785 | 32 |

*Prepared by extruding a physical mixture of EG8200 and Compound A

Oxygen Transmission Rate Units: cc-mil/100 in²-day-atm.

5 EXAMPLE 2

Injection molded samples of polypropylene structural foams are prepared using an Arburg 170CMD brand reciprocating screw injection molding machine equipped with an 18 mm injection cylinder, a mechanical shut-off nozzle, and a plaque mold (cavity dimensions: 65 millimeter x 65 millimeter x 6 millimeter). The mold is fed through a full width, full thickness fan gate.

The specific material formulations in parts per hundred are described in the following table:

| ID | PP | 3150 | Claytone HY | FM1709H | |
|------|----|------|-------------|---------|-----|
| 15 I | | 71.0 | 25.0 | ---- | 4.0 |
| II | | 64.3 | 22.1 | 9.6 | 4.0 |

The materials are obtained from the following manufacturers:

20 H702-35 homopolymer polypropylene (PP): The Dow Chemical Company

Polybond 3150 grafted PP: Uniroyal Chemical

Claytone HY quaternary ammonium treated montmorillonite: Southern Clay Products
(55 wt% inorganic multi-layered silicate material)

FM1709H Blowing Agent: Equistar

25 .The blowing agent is azobisformamide based, and it is in the form of a concentrate in a polyolefin carrier. The PP/Polybond/Claytone HY materials employed in Formulation II were provided as a concentrate (67/23/10) prepared using a 25 mm high speed co-rotating twin screw extruder (a 30 HP Krupp Werner Pfleiderer ZSK Mega Compounder) operating under
30 the following conditions:

Screw Speed: 1000 RPM
Extrusion Rate: 6.64 kg/hr
Torque: 35% of maximum
Barrel Set Temperatures: 150°C
Die Set Temperature: 190°C
Melt Discharge Temperature: 230°C

The respective materials for each formulation were weighed, physically mixed, and then directly fed into the feed throat of the injection molding machine. The molding conditions that are generally employed are summarized below.

| Barrel Set Temp (°C) | |
|----------------------|-----|
| Zone 1: | 182 |
| Zone 2: | 210 |
| Zone 3: | 221 |
| Nozzle: | 221 |

| | |
|----------------------|---------|
| Plasticization Speed | |
| (m/min): | 10 |
| Back Pressure (bar): | 30 (I) |
| | 60 (II) |
| Shot Size (cc): | 18 |
| Fill Time (s): | 0.5 |

| | |
|------------------------|-----|
| Pack Pressure (bar): | 25 |
| Pack Time (s): | 1 |
| Hold Time (s): | 130 |
| Mold Temperature (°C): | 19 |

The foam samples exhibit a density of 26 ± 1 lb/ft³, which represents density reduction of 54% relative to the solid polymer. These foams are subsequently tested for compressive properties by generally following ASTM procedure D1621-94. The results are summarized in the following table.

| <u>ID</u> | <u>Compressive Modulus (ksi)</u> | <u>Yield Stress (psi)</u> |
|-----------|----------------------------------|---------------------------|
| I | 11.7 | 448 |
| II | 12.3 | 536 |

- 5 The nanofilled material exhibited a modulus and yield strength improvement of 5% and 20% relative to the unfilled control. The nanofilled material also exhibits improved post yield properties.

EXAMPLE 3

10 Injection molded samples of glass fiber reinforced polypropylene compounds are prepared using an Arburg 170CMD brand reciprocating screw injection molding machine equipped with an 18 mm injection cylinder and a modified ASTM Type I tensile bar mold. The specific material formulations in parts per hundred is described in the following table:

| <u>ID</u> | Homopolymer Grafted | Claytone | Glass Fiber | |
|-----------|---------------------|----------------|-------------|----------------|
| | <u>H702-35</u> | <u>PB 3150</u> | <u>HY</u> | <u>R22Y-AA</u> |
| 15 D | 67 | 23 | 10 | |
| E | 60 | 21 | 9 | 10 |
| F | 47 | 16 | 7 | 30 |

The materials are obtained from the following manufacturers:

20 H702-35 homopolymer polypropylene (PP): The Dow Chemical Company

Polybond 3150: Uniroyal Chemical

Claytone HY quaternary ammonium treated multi-layered silicate: Southern Clay Products (55 wt% inorganic multi-layered silicate)

25 R22Y-AA: Owens Corning Fiberglas

The PP/Polybond/Claytone HY materials employed in D-F are provided as a concentrate (67/23/10) prepared using a 25 mm high speed co-rotating twin screw extruder (a 30 HP Krupp Werner Pfleiderer ZSK Mega Compounder) operating under the following conditions:

Screw Speed: 1000 RPM

Extrusion Rate: 6.64 kg/hr

Torque: 35% of maximum

Barrel Set Temperatures: 150°C

Die Set Temperature: 190°C

Melt Discharge Temperature: 230°C

The respective materials for each formulation are weighed, physically mixed, and then directly fed into the feed throat of the injection molding machine. The molding conditions that were generally employed are summarized below

Barrel Set Temp (°C)

Zone 1: 182

Zone 2: 204

Zone 3: 215

Nozzle: 215

Plasticization Speed

(m/min): 5

Back Pressure (bar): 20

(200 for Samples C and F)

Shot Size (cc): 16

Fill Time (s): 11

Pack Pressure (bar): 500

Pack Time (s): 60

Mold Temperature (°C): 20

The samples are subsequently tested for flexural properties and coefficient of thermal expansion (CTE) parallel to the length axis by generally ASTM procedures D790 (Method 1 Procedure A) and E831 (-30 °C to 30 °C) respectively. The results are summarized in the following table.

| <u>Sample ID</u> | <u>Flexural Modulus</u> | <u>Yield Strain</u> | <u>Yield Stress</u> | <u>CTE</u> |
|------------------|-------------------------|---------------------|---------------------|------------|
| D | 296.8 | 2.83 | 5230 | 47 |
| E | 472.5 | 2.87 | 6910 | 37 |
| F | 815.3 | 1.69 | 8590 | 27 |

Flexural Modulus in ksi

Yield Strain in percent

Yield Stress in psi

CTE in micro m per m-degree C

EXAMPLE 4

7.5 parts per hundred (pph) Closite 30 brand multi-layered silicate material from Southern Clay Products is blended into 5 gal of Derakane 411-350 (The Dow Chemical Company) at 7 degrees C until homogeneous. 1.5 pph of a mold release agent (Axel PS 125) and 0.3 pph of air release agent (BYK 515) is added, followed by 0.1g of a mixed catalyst containing Peracodox 16N, Trigonox 141, and Trigonox C.

A fiber package consisting of 7 layers (1 = Nexus Veil 110-039, 2 = Glass Matting (M8643, 1.5oz), 3 = Glass roving 46 strands (PPG 2026, 113 yield), 4 = Glass matting, 5 = Glass Roving, 6 = Glass Matting, 7 = Nexus Veil) is impregnated with the resin via a dip bath and pulled through a 15X3 mm flat plate pultrusion die. The curing system consists of three eight inch heating zones (240°F, 280°F, and 280°F). The final parts were 3.94 mm thick, consisted of 52 volume% resin, and 48 volume% glass with a density of 1.4-1.5g/cm³. Test specimens are cut from the final parts and tested with the following results: Tensile strength, 72312 psi; Modulus, 3410191 psi; Strain at break, 2.3%; Elongation at break, 2.28%.

CLAIMS:

1. A process for making an article, the article comprising a nanocomposite polymer, the article selected from the group consisting of a structural foamed polymer, a multilayer polymer film, sheet or tube, a pultrusion structural profile, a compression molded polymer article formed from an extruded fiber reinforced polymer pre-form, a strand foamed polymer article and an article formed by the SCORIM process, comprising the steps of: dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material to form a nanocomposite polymer; the process characterized by the step of forming the nanocomposite article by flowing the nanocomposite polymer to align the planes of the one, two, three, four and five layers of silicate material so that more than one half of the planes have the same orientation within thirty degrees as determined by electron microscopy.
2. The process of Claim 1, wherein the article is a multilayer polymer film, sheet or tube and wherein the number of layers is ten or more.
3. The process of Claims 1-2, wherein the weight percent of the multi-layered silicate material dispersed in the polymer is in the range of from one to twenty percent.
4. The process of Claims 1-2, wherein the weight percent of the multi-layered silicate material dispersed in the polymer is in the range of from two to ten percent.
5. An article made by the process of Claims 1-4.

DECLARATION AND POWER OF ATTORNEY

USA/PCT

As a below named inventor, I hereby declare that:

- (a) My residence and Citizenship are as stated below my name. My P.O. (mailing) address is the same as my residence unless otherwise stated.
 (b) I verily believe I am/we are the original, first and sole/joint inventor(s) of the subject matter that is embraced by and for which a patent is sought

of the invention entitled: **NANOCOMPOSITE ARTICLES AND PROCESS FOR MAKING**

and the specification of which: ☐ is attached hereto (____);
☒ was filed on February 11, 2000 as (44114).
 Application No. PCT/US00/03682
 and was amended on _____

- (c) I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

- (d) I acknowledge my duty under 37 CFR 1.56 to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in 37 CFR 1.56(b). If this application is a continuation-in-part application, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 CFR 1.56(b) that became available between the filing date of the prior application from which priority is claimed in part (f) below, and the national or PCT international filing date of this application.

- (e) I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate listed below or § 365(a) of any PCT international application that designated at least one country other than the United States of America listed below, and also identify below any other foreign equivalent application for patent or inventor's certificate or any other equivalent PCT international application having a filing date before that of the application on which priority is claimed:

| Number | PRIOR FOREIGN APPLICATION(S) Country or PCT | Day/Month/Year Filed | PRIORITY CLAIMED | CERTIFIED COPIES INCL. |
|--------------------------|--|----------------------|--------------------------|--------------------------|
| <input type="checkbox"/> | Additional claims for benefit are attached. | | <input type="checkbox"/> | <input type="checkbox"/> |

- (f) I hereby Claim the benefit under 35 U.S.C. § 119(c) of any United States provisional application(s) listed below, or under 35 U.S.C. § 120 of any United States application(s), or under § 365(c) of any PCT international application designating the United States of America listed below:

| US or PCT Appln. Serial No. | Filing Date | Status at Application Filing Date |
|-----------------------------|---|-----------------------------------|
| <u>USSN 60/119,816</u> | <u>February 12, 1999</u> | <u>Abandoned</u> |
| <input type="checkbox"/> | Additional claims for benefit are attached. | |

I hereby appoint the attorney(s) and/or agent(s) at the following Customer No. to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith. Address all correspondence to The Dow Chemical Company's appointed counsel at:



This appointment, including the right to delegate this appointment, shall also apply to the same extent it is applicable under the laws of the United States of America to any proceedings established by the Patent Cooperation Treaty.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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☒ Additional names and signatures are attached.

